PATENT SPECIFICATION

(54) METHOD AND APPARATUS FOR DISSOLUTION OF A POLYMER IN A SOLVENT

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to the dissolution of polymers in solvents.

One hindrance to the use of high molecular weight polymers as friction-reducing agents for the pipeline transportation of hydrocarbons, such as crude oil and fractions thereof, is that the polymers of a molecular weight sufficiently high to give the desired friction reduction are often difficult to dissolve in the oil or other liquid. Previously, it has been the prevailing practice of the art to charge the polymeric material into a kneader and then very gradually add small amounts of the liquid until a mixture of sufficient consistency is produced to permit discharge into the main liquid body. It has also been a practice to cut, tear or mill the polymeric material into small particles by subjecting the polymer to a severe milling operation or to mastication with mixing equipment, such as kneaders, banburys or extruders. Excessive milling is frequently quite harmful to the polymer, tending to break it down so that a final product is of lower molecular weight and many desirable qualities are lost. As a further drawback, heavy equipment is expensive, power requirements for the use of such equipment are large and batch sizes are generally limited, all of which result in increased blending costs. If the polymer and solvent are agitated with application of heat, the agitation and heating may also lower the molecular weight and, further, will be slow in achieving complete solution. Such a slow procedure is expensive.

One process for dissolution as described in U.S. patent specification No. 2,639,275 involves passing the polymeric material through an extruder and into an apparatus equipped with a series of orifice plates, mixing chambers, and screens, the orifices in the progressive plates being diminishing in diameter, each orifice plate, screen bundle, and mixing chamber being so equipped that a heated pressurized liquid compatible with the polymeric material is admixed with the polymer at these stages. While solution utilizing this apparatus may occur in as short a time as five minutes or less, the process suffers from the serious disadvantage that the polymer is seriously degraded, and particularly in the case of high-molecular weight polymers, is degraded to a point of substantial uselessness for friction reduction.

In accordance with another prior art process as disclosed in U.S. patent specification No. 2,771,458, the size of the polymer particles which are being dissolved are maintained uniform and below 1/4 inch (about 6.3 mm) in diameter, preferably about 1/16 inch (about 1.6 mm), such that high-viscosity blends which are homogeneous and lump-free can be obtained by simple agitation. However, the process requires a high viscosity solvent and may suffer from degradation.

The present invention overcomes or at least reduces the above-described difficulties by providing a method and apparatus whereby a high molecular weight polymer can be efficiently and economically dissolved on a large scale in a solvent without being significantly degraded.

According to the present invention, an apparatus for the dissolution of polymer particles in a solvent comprises a vessel having a liquid space in the lower part thereof and a vapour space in the upper part thereof, means dividing the liquid space into at least two substantially vertical compartments in liquid communication with each other or with one another both above and below the dividing means, baffling means located whereat the compartments are in liquid communication and arranged to deflect polymer particles out of corners, and gas-dispersing means for dispersing a stream of gas into the lower part of at least one but less than all of the compartments.

Also, according to the present invention a method for dissolving a polymer in a solvent, comprises introducing the polymer into the solvent to form a slurry of small polymer particles in the solvent, providing a vapour zone above a liquid zone in a vessel which is partitioned into at least two compartments which are in liquid communication with each other both above and below the partition, dispersing the slurry in the liquid zone, admitting a dispersed stream of gas into at least one but less than all of the compartments, whereby the slurry content of each compartment into which gas is flowing is caused to rise in the compartment, to flow into another compartment over the top of the partition, to descend into the other compartment and flow to back into each of the compartments into which the dispersed stream of gas is introduced, recycling gas from the vapour zone, and removing dissolved polymer and solvent from the liquid zone.

The present invention will be described with reference to the accompanying drawing; in which:—

Figure 1 discloses a batch type dissolution vessel.

Figure 2 discloses a continuous type dissolution vessel with internal baffles.

Figure 3 shows an arrangement of a single draft tube as employed in the apparatus of figures 1 and 2.

Figure 4 shows an arrangement of a plurality of draft tubes which may be employed in the apparatus of figures 1 and 2.

Figure 5 shows another arrangement of a plurality of draft tubes which may be employed in the apparatus of figures 1 and 2.

In accordance with the present invention, agitation to provide dissolution of a polymer in solvent is limited to the "bubbling method" conventionally known as sparging. The primary purpose of sparging in this invention is to disperse the solid polymer particles throughout the solvent. Dispersion is required so as to provide a large polymer surface area for dissolution. Without agitation the polymer particles agglomerate, effectively provide a smaller surface area, and slow the dissolution process. A secondary benefit of sparging is that it also assists in "washing" disentangled polymer molecules away from the polymer particles while the level of agitation is sufficiently low so as not to degrade the dissolved polymer.

The basic method in accordance with the invention for dispersing gas in a liquid contained in a tank or vessel is to introduce the gas through an open-end stand pipe, a horizontal perforated pipe or a perforated plate at the bottom of the tank. Although the size of the bubbles is a function of the diameter of the orifice through which the gas is introduced at low rates, at ordinary gassing rates relatively large bubbles are produced regardless of the size of the orifice.

Perforated pipe or plate spargers employed in accordance with the invention have orifices 1/16 to 1.0 inch (about 1.6 to 25.4 mm) in diameter. The perforated pipe sparger is designed so that the pressure drop across the individual orifices is large compared with the pressure drop down the length of the pipe plus the hydraulic head of the tank contents; otherwise, the orifices most remote from the gas supply may not function. If separate leads are employed for each sparger orifice a high resistance in the leads will again assure uniform sparging through all orifices.

Porous plates, tubes, discs, or other shapes are made for use with the invention by bonding together carefully sized particles of carbon, ceramics, or metal. The resulting septa are used as spargers to produce much smaller bubbles than will result from a simple bubbler. The size of the bubbles formed is proportional to the pore diameter but also to the pressure drop across the septum. At high gas rates coalescence occurs above the septum and poor gas dispersion results.

The position and design of spargers useful with the invention is critical if the best suspensions are to be obtained; in small cylindrical tanks the spargers are shaped concentric with the tank and are located about 1/2 to 3/4 of the distance from the centre to the wall of the tank. Room is left to allow the whole contents of the tank to circulate vertically.

The solvents with which the present invention is most concerned are generally low in viscosity. Thus, crude oil encompasses a preferred embodiment of the present invention inasmuch as it is desirable to incorporate polymer into crude to facilitate pipeline pumping thereof. However, the invention, of course, extends to water, and all fractions of crude oil.

The gas employed for sparging by the present invention is, preferably, nitrogen and light ends from the solvent but may include all non-toxic and otherwise unharmful gases. If the solvent is a hydrocarbon, such gases as methane, propane, and other hydrocarbons are suitable. It is, however, desirable that all oxygen be excluded from contact with the polymer if the polymer is subject to oxidative attack inasmuch as it will have harmful effects upon the polymer. Either centrifugal compressors or positive displacement pumps may be employed to circulate the gas phase. In case of hydrocarbon systems and heated dissolution tanks, some condensation will occur in the pump unit and return lines but this will not have any ill effects and may be eliminated by conventional knock-out pots.

The polymer to be employed in the process generally extends to all polymers of high molecular weight. Examples of such polymers are polyisobutylene, polybutylene, polyisoprene, ethylene-propylene copolymer and polybutadiene. Such polymers have heretofore been very difficult to dissolve without degradation

in the solvents encompassed by the present invention.

Referring now to the apparatus employing the above system of materials, Figure 1 discloses the simplest device anticipated by the present invention. A tank 1, preferably though not necessarily cylindrical, is partially filled with a solvent 9 to leave a vapour space 8 in the top part of the tank 1. Gas or vapour is pumped from the top of the tank 1 by compressor or pump 3 through return line 4 and back into the tank 1 via gas ports 5. The gas bubbles 6 thus introduced into the solvent 9 and dispersed polymer particles rise in the solvent 9 through a draft tube 7 and substantially escape from the solvent at the liquid-vapour interface 2. The gas bubbles 6 in the draft tube 7 decrease the effective density of the fluid in the draft tube 7. The difference in effective densities of the fluid in the spaces inside and outside the draft tube 7 creates a pressure differential at the bottom of the tank 1 between the said spaces. This pressure differential generates flow of the solvent 9 and dispersed polymer in the direction as indicated by the arrows. In the example cited the flow of solvent and dispersed polymer is up in the draft tube 7 and down in the annular space 10 outside the draft tube 7.

In figure 2 of the drawings, an apparatus for continuous operation is disclosed. Solvent with dissolved polymer is withdrawn continuously from tank 30 via relatively large outlet 31 which is designed to have a slow flow rate which will not tend to remove undissolved polymer particles from the dissolution vessel. Above the liquid-vapour interface 39 a vapour space 45 is present. Meanwhile, polymer is continuously introduced via inlet 32 to the tank 30 which has a flame arrestor blow-off valve 33, and oil or other solvent is admitted to the tank through an inlet 34. Fluid flow may be reversed in outlet 31 and inlet 34 to clean filters. Gas is continually circulated through the contents of the tank 30 by compressor or pump 35 via gas return line 36 and into gas ports 37 upwardly through draft tube 38. Solvent 43, dispersed polymer particles and gas bubbles 42 flow in an upward direction in the space inside the draft tube 38 as indicated by the arrows and then down through the annular space 44 outside the draft tube 38 after being deflected by top baffles 40. Such baffles 40 are very useful for polymers less dense than the solvent. On reaching the bottom of the tank wall, the polymer is diverted back into the draft tube 38 by bottom baffles 41 which are most useful for polymers more dense than the solvent. In general, the said baffles serve to keep the polymer from collecting in corners of the vessel and to keep the polymer is continuous flow. The position of the draft tube 38 within the tank 30 is generally controlled so that the distance between the edge of the draft tube 38 and the

said baffles is equal to or less than the distance between the draft tube 38 and the wall of the tank 30. This ensures a thorough sweeping action about the edges of the draft tube 38 and eliminates any dead spots in the tank 30.

Figures 3, 4 and 5 disclose various patterns which may be employed for the draft tubes. The simplest arrangement is shown in figure 3, which discloses a single draft tube 15 extending through the tank 16, gas being admitted into the draft tube 15 through gas ports 17. In figure 4 a somewhat more complex design is disclosed, wherein three concentric tubes 18, 19, 20 are arranged within the tank 21, viz. respectively an inner tube 18, a middle tube 19 and an outer tube 20. Gas ports 22 are present in the bottom of the tank 21 and within the inner tube 18. Furthermore, gas ports 23 are present in the bottom of the tank 21 and between outer tube 20 and middle tube 19. During normal use of this embodiment gas rises in the inner tube 18 to circulate the solvent up the tube 18 and down the middle tube 19; likewise, gas is admitted into the outer tube 20 to circulate solvent downwardly both outside the outer tube 20 and inside the middle tube 19. In the embodiment of figure 5, six non-concentric draft tubes 24 are arranged in a tank 25, wherein gas is admitted through gas ports 26 up through the tubes 24 and down through the rest of the tank 25 to ensure continuous circulation.

To maintain good dispersion and thus achieve rapid dissolution, the solvent velocity must exceed the terminal polymer particle velocity in the solvent in absence of solvent motion. Sparging rates for achieving sufficiently high solvent velocities depend upon the viscosity of the solution, polymer and solvent density, and tank and draft tube dimensions but should be such that the superficial velocity is between 0.01 and 5.0 feet per minute (about 0.3 cm and 152 cm per minute). Superficial velocity is defined as the gas flow rate divided by the flow area. In tanks without draft tubes, this area is the tank cross-section. If draft tubes are employed, the area is the cross-section of that portion of the tank where upflow of the gas occurs. Usually the upflow area will be between one-quarter and one-half of the total tank cross-section. Draft tubes allow for a more efficient dispersion and represent the preferred method of this invention. As above noted, more than one draft tube may be used and they may be arranged in various patterns as shown in figures 4 and 5 above discussed. The sparging is, preferably, accomplished through a multiplicity of gas ports. Individual gas ports should not exceed 1.0 inch (25.4 mm) in size and, preferably, should be 1/4 inch (6.3 mm) in diameter. Of course, as above noted, porous septum may be employed instead of simple ports. However, where the gas ports are employed they should

be separated so as to prevent coalescence of gas bubbles from different ports. Thus, the separation distance is a function of solvent height in the tank and should be such that the distance between ports is 1/40 to 1/2 the solvent height.

The polymer particles may be either less or more dense than the solvents. For instance, an 8×10^4 molecular weight polyisoprene crumb, initially is less dense but later becomes more dense than the crude oil used as a solvent. The low initial effective density is due to air trapped in the crumb and its release as the crumb becomes solvated with solvent. The buoyant and more dense particles tend to collect and agglomerate in regions of the dissolution tank where flow is zero and very slow. Such regions occur in tank corners and at the solvent top surface near the tank wall. Baffles 40 and 41, installed as shown in figure 2, prevent such an occurrence. The polymer may be such that its molecular weight is in the range 5×10^4 to 20×10^4, although the method of the present invention is not limited to the use of such polymers.

Concentration of polymer to be dissolved in the batch process is determined by the viscosity of the final solution. The highest concentration is such that the final viscosity does not exceed about 200 centipoises at a shear rate of 100/secs. For high molecular weight polymers this concentration is 0.5 to 2% by weight, based on the total weight of polymer and solvent. The dissolution rate is almost a linear function of the ratio of surface area to mass of polymer. Thus, the smaller particles have a faster dissolution rate. Small particles may be prepared with conventional shreaders, extruded and then cut as shown in U.S. patent specification No. 2,771,458, or they may be obtained in a crumb form. Crumb is preferred to cut or shreaded material since crumb has a highly convoluted surface and offers a larger surface area per unit volume than the other particles. The size particles to be employed in this process ranges from micron size, as for example a powder, to 1.0 inch (25.4 mm) size crumb or to cut particles. The dissolution rate is further enhanced by the choice of a good solvent of low viscosity in the range of 0.5 to 20 centipoises, and elevated temperatures.

If higher than available temperatures are desired, the solvent may be preheated or the dissolution tank may contain heating elements. In the case of heating elements the heating surface temperature must be limited so as not to degrade the polymer. In the case of polyisoprene, this temperature ranges from about 200°F to 300°F (93° Centigrade to 149° Centigrade). Further, the temperature in the tank should at all times be less than the first boiling point of the solvent to prevent significant loss of solvent in low-pressure dissolution tanks.

The pressure maintained in the dissolution vessel is preferably in the range of from 0 inch (0 mm) of water to about 3/4 inch (19 mm) of water, with pressure of the order of about 1/2 inch (12.7 m) of water being preferred. Higher pressures, i.e., in the order of several psia or more, may be employed but are not generally recommended because they increase the hazards and expenditures of capital required to provide the reactor without corresponding improvements in the process.

In the following Table the results of several runs with polyisoprene and polyisobutylene in crude oil are disclosed in order to illustrate but not limit the invention.

TABLE

Polymer	Solvent	Temp.	Solvent viscosity	Dissolution tank diameter	Draft tube	Sparge rate*)	Particle size	Conc. (%w)	Initial mol. wt.	Final mol. wt.	Time to dissolve (hrs)	Remarks
Poly-isoprene	Crude oil	90°F (32°C)	2 cp	18" (46 cm)	yes	0.9 ft/min. (27 cm/min.)	3/8" (9.5 mm) crumb	0.92	8×10^6	7.3×10^6	120	
Poly-isoprene	Crude oil	90°F (32°C)	2 cp	18" (46 cm)	yes	2.5 ft/min. (76 cm/min.)	3/8" (9.5 mm) cut	0.94	8×10^6	7.2×10^6	160	
Poly-isoprene	Crude oil	70°F (21°C)	4 cp	12" (30 cm)	no	0.5 ft/min. (15 cm/min.)	1/4" (6.3 mm) crumb	2.00	8×10^6	8×10^6	47	
Polyiso-butylene	Crude oil	140°F (60°C)	1 cp	23" (58 cm)	no	0.7 ft/min. (21 cm/min.)	1/4" (6.3 mm) cut	0.85	4.7×10^6	4.5×10^6	84	Approx. ½ of polymer dissolved. Run terminated

*Superficial velocity

In the present invention specific relationships of vessel dimensions and flow rates during operation of the process are important in designing the apparatus. For example, it is preferred that the cross-sectional areas of the compartments in which liquid flows in opposite directions be such that the pressure drop due to the flow in them is approximately equal. Thus, it is desirable that the cross-sectional area of the annular space outside the tubes be larger than that of the tubular space because the annular space has more surface friction. In single draft tube systems a useful range for the ratio of draft tube to annular cross-sectional area is between 0.25 and 1.5, while 0.48 is the preferred ratio. Usually it is undesirable to have the total cross-sectional area of compartments in which flow is in one direction more than approximately two times as great as the cross-sectional area of compartments in which flow is in the opposite direction. To provide for unobstructed circulation of the solvent slurry from one compartment into another, it is preferable that the liquid space above the draft tube and the liquid space below the draft tube in a vessel of

circular cross-section each be approximately equal to the distance between the draft tube and tank wall. It is preferred that the compartments of the dissolution vessel be relatively elongated.

WHAT WE CLAIM IS:—

1. A method for dissolving a polymer in a solvent, comprising

Introducing the polymer into the solvent to form a slurry of small solid particles in the solvent, providing a vapour zone above a liquid zone in a vessel which is partitioned into at least two compartments which are in liquid communication with each other both above and below the partition,

dispersing the slurry in the liquid zone,

admitting a dispersed stream of gas into at least one but less than all of the compartments, whereby the slurry content of each compartment into which gas is flowing is caused to rise in the compartment, to flow into another compartment over the top of the partition, to descend into the other compartment and flow to back into each of the compartments into which the dispersed stream of gas is introduced,

recycling gas from the vapour zone, and

removing dissolved polymer and solvent from the liquid zone.

2. The process of claim 1, wherein the method is carried out continuously by recirculating gas continuously through the compartment and continuously withdrawing dissolved polymer and solvent and continuously adding polymer particles and fresh solvent.

3. The method of claim 1, wherein the dissolution is carried out as a batch process.

4. The method of claim 1, wherein the concentration of dissolved polymer in solvent is 0.5 to 2%, by weight, based on the total weight of polymer and solvent.

5. The method of claim 1, wherein the gas introduced into the dissolution vessel is a non-oxidizing gas.

6. The method of claim 1, wherein the polymer is polyisoprene of about 8×10^5 molecular weight in the form of crumb.

7. The method of claim 6, wherein the crumb varies in particle size from micron size to 1.0 inch (25.4 mm) size.

8. The method of claim 1, wherein the viscosity of the solvent is in the range 0.5 to 20 centipoises.

9. The method of claim 1, wherein the polymer is polyisoprene and the dissolution vessel is heated to about 200°F (93° Centigrade).

10. The method of claim 1, wherein the molecular weight of the polymer is in the range 5×10^5 to 20×10^5.

11. The method of claim 1, wherein the gas is introduced through individual gas ports of less than 1.0 inch (25.4 mm) in size.

12. The method of claim 1, wherein the gas is introduced through gas ports of 1/16 to 1.0 inch (1.6 mm to 25.4 mm) in diameter.

13. The method of claim 1, wherein the separation distance between gas ports through which the gas is introduced ranges from 1/40 to 1/2 the solvent height in the dissolution vessel.

14. The method of claim 1, wherein the gas is dispersed by porous septa.

15. An apparatus for the dissolution of polymer particles in a solvent, comprising a vessel having a liquid space in the lower part thereof and a vapour space in the upper part thereof, means dividing the liquid space into at least two substantially vertical compartments in liquid communication with each other or with one another both above and below the dividing means, baffling means located whereat the compartments are in liquid communication and arranged to deflect particles out of corners, and gas dispersing means for dispersing a stream of gas into the lower part of at least one but less than all of the compartments.

16. The apparatus of claim 15, wherein the ports through which the gas is introduced do not exceed 1.0 inch (25.4 mm) in size.

17. The apparatus of claim 15, wherein the ports through which the gas is introduced are 1/16 to 1.0 inch (1.6 mm to 25.4 mm) in diameter.

18. The apparatus of claim 15, wherein the ports through which the gas is introduced are separated by a distance which is from 1/40 to 1/2 the height of the solvent in the dissolution vessel.

19. A method of dissolving a polymer in a solvent substantially as hereinbefore described with reference to figure 1 or 2, together with any one of figures 3 to 5, of the accompanying drawings.

20. An apparatus for the dissolution of polymer particles in a solvent substantially as hereinbefore described with reference to figure 1 or 2, together with any one of figures 3 to 5, of the accompanying drawings.

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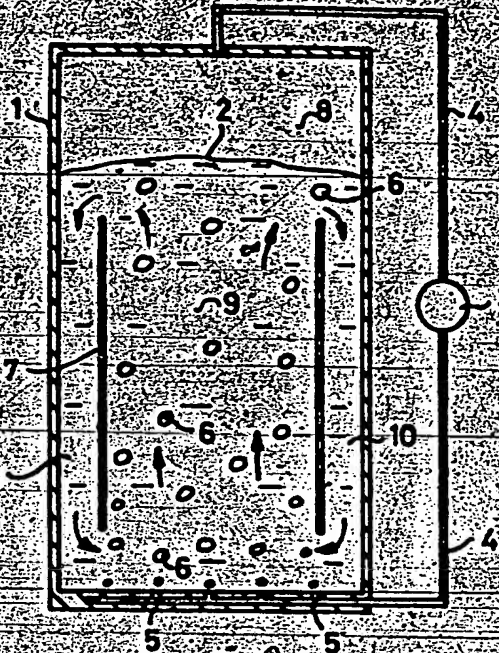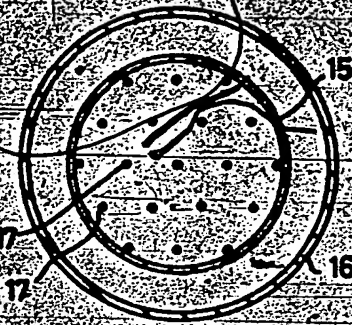London, SE1 7NA.
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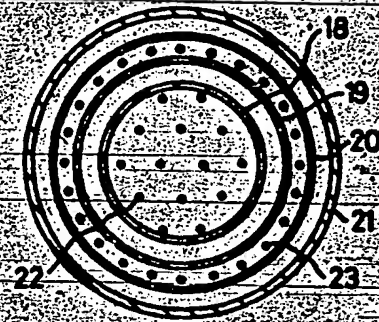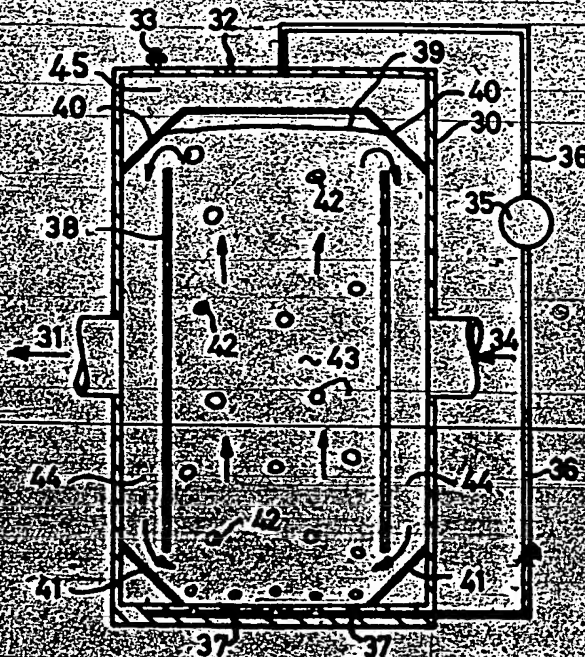1 452 146   COMPLETE SPECIFICATION
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the Original on a reduced scale.

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5